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11. CONTE	POLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
	. Army Research Office		3/18/92
2	Office Box 12211		13. NUMBER OF PAGES
14. MONIT	ORING AGENCY NAME & ADDRESS(If different	from Controlling Office)	15. SECURITY CLASS. (of this report)
l			Unclassified
į.			154. DECLASSIFICATION/DOWNGRADING SCHEDULE
			SCHEUGE
16. DISTRIBUTION STATEMENT (of this Report)			
Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abetract antered in Block 20, if different from Report)			
NA.			
110			
18. SUPPLEMENTARY NOTES			
The view, opinions, and/or findings contained in this report ar:			
those of the author(s) and should not be construed as an official  Department of the Army position, policy, or decision, unless so			
designated by other documentation.			
19. KEY WORDS (Continue on reverse elds it necessary and identify by block number) Tribology, Functionally Terminated Oligomers, Langmuir-Blodgett Films			
26. ABSTRACT (Cartinus on reverse atthe H recessory and Identify by block number)			
A research outline is described for an investigation into the applicability of Langmuir-Blodgett films of functionally terminated oligomers as specialized			
lubricants.			

# TRIBOLOGY OF FUNCTIONALLY—TERMINATED OLIGOMER FILMS

Technical Report No. 2

C.L. Mirley, J.T. Koberstein

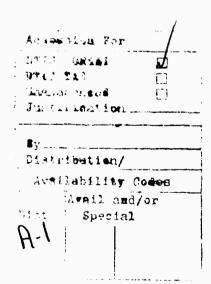
March 1992

U.S. Army Research Office

Contract Number: 27863-MS

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# TRIBOLOGY OF FUNCTIONALLY-TERMINATED OLIGOMER FILMS

Dissertation Prospectus for the Ph.D. Degree

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University of Connecticut
January 10, 1992

## INTRODUCTION AND BACKGROUND

The word tribology is derived from the Greek word for rubbing, *tribos*<sup>1</sup>, and refers to the science and technology of interacting surfaces in relative motion. The nature of these interactions is generally addressed under the subject of friction behavior, while the consequences or responses of a material to these interactions are the subject of wear behavior. However, these two subjects are closely related and are important from both a theoretical and economic point of view.

Whenever two solid bodies in contact are forced to move relative to one another there develops a resistance to the motion which we call friction. Friction is essentially an energy consuming process which can be reduced but never entirely eliminated. The basic law of sliding friction was first put forth by Amonton in 1699 who defined the friction coefficient  $\mu$  as being equal to the ratio of the frictional or tangential force to the normal force. This has been proven to hold for many different solid/solid systems but does little to enhance our understanding of friction behavior based on material properties.

Bowden and Tabor <sup>2</sup> in the 1930's initiated a more systematic approach to the study of friction mechanisms. The realization that all surfaces are rough on a microscopic scale lead to their 'adhesion-shearing' model for friction. In this model, a solid surface is composed of sharp peaks (asperities) and valleys. When two sliding surfaces come into contact, the asperities on each surface interact and form welded junctions. The frictional force therefore depends on the shear strength of these junctions as well as the true area of contact between the sliding surfaces. Consequently the friction coefficient has components due to adhesion and to deformation of surface asperities. A more successful model for sliding friction was put forth by Suh and Sin <sup>3</sup> and treats the friction coefficient as a sum of three terms: adhesion, deformation, and ploughing. A theory for friction behavior based on surface energy has also been proposed by Lee.<sup>4</sup>

Studies on polymer materials such polyethylene, PTFE, and polystyrene have indicated that the frictional characteristics of these materials are influenced by their molecular structure.<sup>5,6</sup> Factors such as crystallinity, molecular symmetry, and molecular orientation are important in determining both the magnitude of the friction coefficient and the type of wear behavior observed. The friction behavior of other materials such as graphite and molybdenum disulfide, which are widely used as solid lubricants, has also been linked to their unique molecular structures.

With the advent of such instrumentation as the surface force apparatus and the atomic force microscope, the tribology of materials can now be studied at the atomic or molecular level.<sup>7,8</sup> The goal of these types of investigations is to develop a microscopic understanding of tribology so that rational designs for tribology-based applications can be formulated rather than relying on those that are empirically derived.

Wear can be generally described as the progressive loss of material from the surface of a body as a result of solid-solid interactions with the surface. The types of wear behavior observed among

different materials have been classified into two groups: <sup>3,9</sup> 1) Those processes dominated by the mechanical behavior of the materials under a given load. This includes sliding or adhesive wear, abrasive wear and fatigue wear; 2) Wear processes that are controlled by chemical and thermally activated processes. These include oxidative, solution, and corrosive wear. There is usually more than one wear mechanism occurring at any given time during solid-solid motion which makes it rather difficult to determine the exact causes of wear. Other factors such as temperature, humidity, and the presence or absence of lubricants also affects the wear behavior of materials. Whatever the causes, the reported economic costs of wear are enormous.

The parameter measured most often in wear investigations is the wear rate for which there are two types. The first is the depth wear rate,  $W_h=h/d$ , where h is the thickness of material removed or thickness of the wear track and d is the slide distance. It is preferable to divide h by the slide distance rather than time in order to eliminate the effects of sliding velocity. The second is the volumetric wear rate,  $W_v=V/dL$ , where V is the wear volume and L is the applied load. The wear volume has also been equated to the inverse of the material hardness. The proportionality factor between the wear volume and hardness, called the wear coefficient K, is also used as a measure of wear.

To explain some of the wear mechanisms cited previously, a number of theories have been developed. For sliding wear, the adhesion theory <sup>2</sup> which is the same as that for friction, was first proposed. In this theory, the wear of materials is primarily due to shearing of the surface asperities that are adhered together. The major problem with the theory was that it violated the law of energy conservation and so could not be used to form the basis for designing wear resistant materials. The delamination theory for sliding wear <sup>3</sup> was more successful at modeling this type of wear because it took into account the fact that the primary mode of energy dissipation during sliding wear is through deformation of the region beneath the asperities. This leads to crack nucleation and propagation and eventually to delamination. Abrasive wear has been modeled as a cutting process and Rabinowicz's theory <sup>3</sup> states that the volume of material cut is equal to the volume displaced by a wear particle. In this case the wear coefficient is directly related to the geometry of the asperity and to the friction coefficient.

In order to reduce the damage to sliding surfaces caused by friction or wear processes, lubricants are often used. To date, gases, liquids, and solids have all been used to reduce friction and wear. The basic considerations in designing lubricant systems are as follows: 1) Distance between the surfaces; 2) Forces acting on the surfaces; 3) The chemical and physical nature of the surfaces. 10

One type of lubricant which has important technological applications is thin organic films. <sup>11</sup> These lubricants are especially useful in areas where the distance between moving surfaces is extremely narrow. For example, to prevent mechanical failure in magnetic storage media such as computer hard disk drives, a thin surface layer (usually less than 100 Å) of a fluorocarbon material is coated on the disk. <sup>12</sup> In order for this lubricant to be effective, however, the thickness of these films must be

precisely controlled. Films that are too thick cause the head to stick to the disk thereby causing damage whereas films that are too thin cause the disk and head to wear rapidly. Migration of the lubricant during disk use, which leads to dry tracks in the center of the disk, can also be a problem. A way to overcome these difficulties may be to use Langmuir-Blodgett (LB) or self-assembled (SA) films. 11,14,15 The methods for preparing these films are quite different but the results are very similar i.e. oriented monolayer or multilayer molecular assemblies.

LB films are named after the scientists who developed the process for preparing thir. films from water surfaces: Irving Langmuir and Katherine Blodgett. The effects of monolayers at air/liquid interfaces have been known at least since the time of Aristotle<sup>15</sup>, and have been studied by such notable individuals as Benjamin Franklin and Lord Rayleigh. Not all substances however are capable of forming insoluble monolayers at the air/water interface but those that are can be classified generally into two groups: polymeric and nonpolymeric.<sup>14</sup>

Nonpolymeric compounds are the 'classical' monolayer materials and their ability to form monolayers at the air/water interface is due to their amphiphilic properties; one portion of the molecule is attracted to the water or subphase while the other usually larger portion of the molecule is repelled by it. The balance between these two forces determines whether or not a molecule will form an insoluble monolayer. Examples of these materials are fatty acids (greater than  $C_{10}$ ), alcohols, amines, aromatic hydrocarbons, and heterocyclic compounds.

In the case of polymeric materials, somewhat different criteria apply for monolayer film formation. Unlike the 'classic' monolayer materials, a high degree of insolubility is not required. Instead it is only necessary that the monomer units of the polymer have sufficient attraction for the subphase to overcome bulk cohesion effects. <sup>14</sup> Therefore it is possible to produce polymer monolayers from materials that are water soluble. Polymer monolayers can be prepared as preformed films or polymerized *in situ* after being deposited onto a substrate. Examples of these materials include poly(acrylates), PMMA, polysiloxanes, diacetylenes, and some polypeptides.

In general, to prepare LB films a teflon or teflon-coated trough with a movable barrier is first filled with ultraclean water. The pH of the water may be adjusted by the addition of buffers, or metal salts may also be added to the subphase to help condense the film. A very dilute solution of the monolayer material is prepared in a volatile solvent and a small amount added dropwise to the water surface. After the solvent has completely evaporated, the barrier is slowly compressed until the monolayer has reached a highly compact or solid-like state. The barrier is then stopped and the substrate to be coated is passed through the monolayer/water interface. By dipping the substrate repeatedly, layers of the film can be built up.

SA films are formed by the spontaneous adsorption of a molecule from an organic solvent onto an appropriate substrate. Only certain combinations of compounds and substrates yield SA films e.g. organochlorosilanes on hydroxylated surfaces, alcohols and amines on platinum, carboxylic acids on aluminum oxide and silver, and more recently alkanethiols and sulfonated polymers on gold and silver

substrates. <sup>11, 16, 17</sup> In each of these examples, the molecules have a head group that can chemisorb onto the substrate exothermically. The strong molecular-substrate interactions bind the head group to specific sites on the substrates via covalent or ionic chemical bonding. These bonds have associated energies on the order of tens of kcal/mol. Due to the exothermic nature of these interactions and because of chain-chain interactions (Van der Waals or long range electrostatic in nature), the molecules are adsorbed spontaneously onto the substrate surface from solution and are then thought to migrate to form fairly close packed structures. The overall results are similar to LB films in that molecules are anchored to a substrate with their chain axes in some fixed orientation relative to the substrate surface. One group of investigators, working with organochlorosilanes, found that the tilt angle of the oriented SA monolayers could be controlled by depositing the films from a mixed solution containing molecules that had long and short hydrocarbon chain segments. <sup>18</sup>

Studies on the tribology of LB and SA films have mainly involved materials that have  $C_{10}$  to  $C_{24}$  hydrocarbon chains and hydroxyl, acid, amine, chlorosilyl, or thiol head groups. <sup>11</sup>, <sup>15</sup>, <sup>19</sup> The friction and wear behavior of their partially fluorinated analogs have also been investigated. Studies done by Bowden and Tabor <sup>2</sup>, and later extended by Briscoe and Evans <sup>20</sup>, with sliding mica surfaces showed that the presence of a single fatty acid LB monolayer on each surface was sufficient to reduce the coefficient of friction by a factor of 20 and the wear rate by more than 10,000. The magnitude of the interface shear strength and hence the friction coefficient was found to be relatively insensitive to the chain length but partial fluorination of the chains increased the coefficient of friction.

A similar study by Novotny et. al.  $^{21}$  carried out with LB films of cadmium arachidate ( $C_{20}$ ) on silicon surfaces showed that the best durability was found when the ceramic slider and silicon surface were both covered with a single monolayer. By using microellipsometry it was observed that, for multilayers, all the layers except the layer bound to the substrate were removed after about one hundred sliding cycles. This is in contrast to the results found by Briscoe and Evans where the durability of mono- and multilayers of behenic acid ( $C_{22}$ ) were comparable.

DePalma and Tilman<sup>22</sup> have studied the tribology of SA monolayers consisting of  $C_{11}$  and  $C_{18}$  trichlorosilanes on smooth silicon surfaces. A fluorinated analog of the  $C_{11}$  compound was also studied. Using glass beads as the slider material, it was found that the friction coefficient and wear rate was lowest for the  $C_{18}$  monolayer and highest for the fluorinated  $C_{11}$  SA film.

#### **MOTIVATION AND SCOPE**

LB and SA films not only have important tribological applications, as indicated previously, but are important as model systems for studying boundary lubrication. Boundary lubrication occurs when two surfaces are moving under high loads and low-to-moderate sliding speeds. In this regime, the lubricating fluid film thickness falls below the average surface roughness and the interaction between the contacting surfaces becomes important in determining the friction behavior of the system. Despite

the extensive work and developments made in understanding the macroscopic properties of boundary lubrication, the microscopic behavior of the fluid film molecules at the solid interface is not well understood. Such factors as the role of interactions between the surfaces and the molecules, conformation of the molecules on the surface, molecular transfer from one surface to another, and their migration on solid surfaces need to be addressed. LB and SA films seem ideally suited to answer some of these questions due to the fact that with these materials one is able to control molecular orientation, packing, chemical structure, and film thickness.

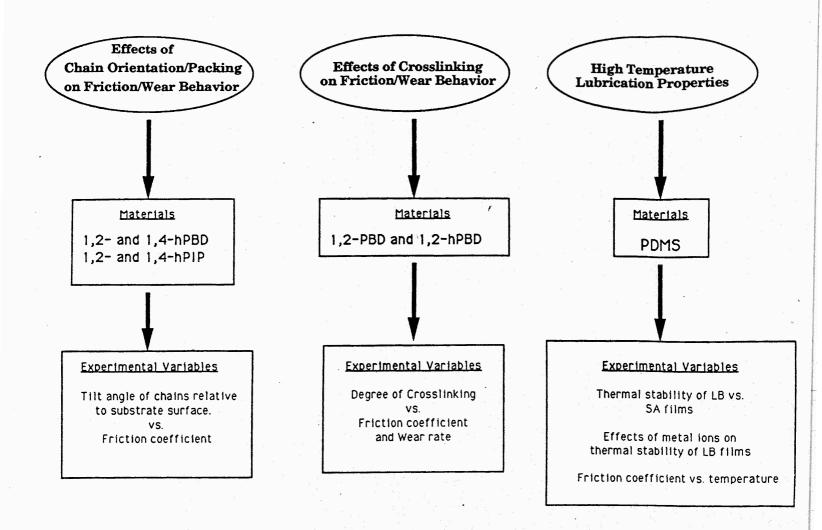
The objective of this proposal is to investigate the friction and wear behavior of a novel class of thin film formers called functionally-terminated oligomers (FTO's) and to use them to study the effects of chain orientation, crystallinity, crosslinking, endgroups, and high temperature on boundary lubrication. Figure 1 shows a schematic overview of the experiments planned for these studies.

There are several advantages to using oligomers as LB or SA, films. First, the materials are polymers but are below their entanglement molecular weight. In the case of LB films, this means having the relative ease of film fabrication as found with smaller molecules while retaining the properties of polymeric monolayers. Secondly, film thickness for a single monolayer can be controlled over a larger range than that attainable with polymer or small molecule film formers. Thirdly, by using the techniques of polymer synthesis, a virtual 'design palette' of FTO's can be made to incorporate such features as polymerizable or fluorescent side groups, various backbone materials, or various endgroups into the molecule.

To study the effects of chain orientation and packing on boundary lubrication, LB films will be prepared from FTO's based on hydrogenated 1,2- and 1,4-polybutadiene (PBD) and 1,2- and 1,4-polyisoprene (PIP). Figure 2 shows the chemical structure for these materials. For this series of materials, the bulkiness of the side groups increases in the following order: 1,4-PBD < 1,4-PIP < 1,2-PBD < 1,2-PIP. This should affect the tilting and/or packing of the molecules when they are deposited onto substrates as LB films. The average tilt angle will be determined by GIR or ATR-IR and the affect on the friction coefficient will be determined using a commercial computer-automated pin-on-disk tribometer. A nonhydrogenated 1,2-PBD FTO will be used to determine what effect crosslinking has on the friction and wear behavior as compared to the hydrogenated analog. The nonhydrogenated PBD FTO has vinyl side groups that can be polymerized after LB film deposition by ultraviolet light. The effectiveness of these FTO's as boundary lubricants will be investigated by using substrates that have different degrees of surface roughness. The surface roughness will be evaluated using scanning tunneling microscopy. Lastly, by changing the endgroups that are exposed to the surface of the PBD films, the effect of endgroup polarity on the friction coefficient will be studied.

Because of its good thermal and oxidative stability, FTO's of polydimethylsiloxane (PDMS) will be tested to determine their high temperature lubrication properties. Materials to prepare both Langmuir-Blodgett and self-assembled films will be available. The effect of incorporating different metal ions into the LB films on their thermal stability will be investigated. The effect of substrate composition on the thermal stability will also be investigated. Comparisons of the high temperature

FIGURE 1: Shematic Diagram of Experimental Procedure.



# FIGURE 2: Molecular Structures for PBD, PIP and PDMS Functionally-Terminated Oligomers.

-(CH<sub>2</sub>-C=CH-CH<sub>2</sub>-)<sub>n</sub> CH<sub>3</sub>

1,4 polybutadiene

1,4-polyisoprene

1,2-polybutadiene

1,2-polyisoprene

$$\begin{array}{c} \mathsf{CH_3} \\ \mathsf{COOH\text{-}CH_2CH_2CH_2f} \\ \mathsf{Si} \ - \ \mathsf{O} \ \frac{1}{\mathsf{J_n}} \ \mathsf{CH_2CH_2CH_2\text{-}COOH} \\ \mathsf{CH_3} \end{array}$$

Di-acid Terminated PDMS

friction and wear behavior between PDMS LB and SA films will be made to determine if there are any significant differences between these film preparation methods. The following equipment will used for these studies: pin-on-disk tribometer to monitor the friction coefficient; an ellipsometer to monitor changes in film thickness or homogeneity; XPS and FTIR to monitor changes in film composition; thermal gravimetric analysis (TGA) to determine film loss as a function of temperature. The tribometer has a high temperature option and is capable of reaching temperatures up to 600 °C. Fabrication of LB films will be carried out using an LB trough.

## **EXPERIMENTAL**

#### **Materials**

Mono-acid terminated oligomers of hydrogenated 1,2- and 1,4-PBD, 1,2- and 1,4-PIP will be synthesized anionically in our lab by Dr. R. Bhatia. Nominal  $M_n$  will be 1300-1500 g/mole. Both hydrogenated and nonhydrogenated di-acid terminated 1,2-PBD is available commercially from Nisso Nippon Soda C., Ltd through Nissho Iwai American Corp. Di-acid terminated PDMS has been synthesized by the equilibration method and will be fractionated using supercritical fluid extraction by Phasex Corp. Nominal  $M_n$  will be in the range of 900-3000 g/mole. Figure 1 shows the chemical structure of this compound. Di-amine and thiol PDMS samples have been obtained from Shinetsu and Toshiba Corp. Nominal  $M_n$  are 2000-7000 g/mole. Monofunctional acid terminated PDMS will also be synthesized anionically in our lab by Dr. R. Bhatia.

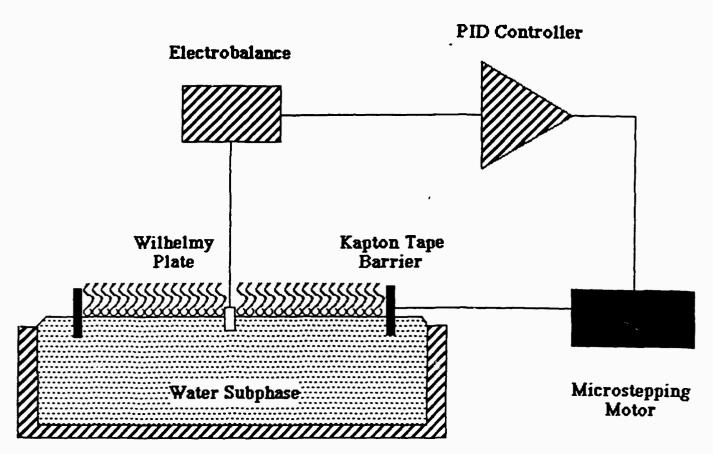
A variety of substrates for the LB and SA films will be used. These include silicon, silicon carbide, glass, silver and gold coated glass. Si(111) wafers have been received from the Motorola University Support Program. A metal evaporator equipped with a thickness monitor and capable of depositing very thin films is available for preparing the metal on glass substrates.

Ultrapure water for the Langmuir trough is provided by a Millipore Super-Q water polishing system. Water with a specific resistance of at least 18 M $\Omega$ cm is supplied on demand.

#### Equipment

Langmuir Trough: A computerized LB trough has been designed and constructed in-house to fabricate thin films by the Langmuir-Blodgett technique. Figure 3 shows a schematic diagram of this equipment. The trough consists of an FEP coated stainless steel tank of approximately 10 liter capacity. The system has a removable barrier of teflon-coated polyimide Kapton tape. Barrier compression speeds from 2-480 mm/min are available while compression ratios of 20 are achievable. The surface pressure is monitored during compression using the Wilhelmy plate method by using a Perkin-Elmer microbalance. The microbalance is part of a feedback control system which allows the user to maintain constant surface pressures during substrate coating. An AT&T 6300 computer controls the software and the stepping motor controls for the feedback control loop. The software also allows for real time plotting of the pressure-area isotherm as well as calculation of film transfer ratios. A dipping device for substrate coating is also available with dipping speeds of 1-100 mm/min. The trough is housed in a class 10

FIGURE 3: Shematic Diagram of Langmuir Trough.



Trough: FEP Coated Steel

laminar flow hood inside the clean room.

Friction Testing: Friction measurements will be carried out on an ISC-200 pin-on-disk tribometer from Implant Sciences. This is a computerized continuous motion apparatus capable of testing materials up to temperatures of 600 °C. Several different types of inert atmospheres may also be used with this equipment. Substrates that are up to 3 inches in diameter can be accommodated and rotational speeds from 0-150 rpm are available. There are several computer programs available as well. The program PC Strip Chart displays and stores the raw friction data and is capable of replotting the data in a variety of different forms. The Hertz program computes the contact pressure of the normal load based on the pin contact area, the elastic modulus, and Poisson ratio for the pin and disk materials. This instrument has been designed to be used as part of the ASTM G99 pin-on-disk friction testing protocol.

# Techniques

Ellipsometry: The thickness of LB and SA films will be determined by using a variable angle spectroscopic ellipsometer (J. A. Woollam Co.). This technique reflects monochromatic polarized light from the surfaces of substrates that are coated with a thin film. The properties of the reflected light are used to determine the refractive index and thickness of the surface coating. The ellipsometer can also be used to model surface roughness as well as film homogeneity. This technique will also be used to monitor changes in wear track film thicknesses during friction measurements.

X-ray Photoelectron Spectroscopy (XPS): This technique will provide compositional information on the LB and SA films. In XPS, a sample is bombarded with monochromatic x-ray radiation which interacts with the core electrons of the atoms present in the sample. Through a series of cascade reactions, electrons are emitted and detected by the XPS. The kinetic energy or alternatively the binding energy of the emitted electrons can be used to identify the atomic element from which it came. The kinetic energy is also sensitive to the atoms that are bonded to the electron emitting atom and so can be used to quantify chemical species. Varying the take off angle of the emitted electrons changes the sampling depth of the emitted photoelectrons allowing composition profiles to be contructed. By using the values of the mean free paths of the electrons and either a substrate attenuation or substrate overlayer model, the thickness of the sample can be calculated.

Fourier Transform Infrared Spectroscopy: To determine the orientation of the FTO's in the LB or SA films, grazing incidence reflection (GIR) or attenuated-total reflectance (ATR) IR will be used. In GIR, reflection-absorption spectra are obtain for films coated on highly reflective surfaces at grazing angles of incidence (75-80° to substrate normal). At these angles, only the component of the IR radiation which is perpendicular to the plane of the substrate is measurable. Therefore molecules that have their vibrating dipoles aligned with the perpendicular IR electric vector will show maximum absorbance and those that are tilted from the normal by an angle  $\emptyset$  will have their absorption diminished proportionately to  $\cos^2 \emptyset$ . Band intensities can then give information about the orientation of the FTO's with respect to the substrate surface.<sup>23</sup> It is also possible to use ATR-IR to determine average tilt angles in LB or SA films. In this technique, the films must be coated onto ATR crystal cells

(silicon, germanium, KRS-5) and polarized IR radiation is internally reflected through the cell. The dichroic ratio D, which is the ratio of the absorbance for the perpendicular to the parallel polarized radiation, can be calculated versus the tilt angle. <sup>11</sup> The dichroic ratio is then measured and the tilt angle read from the calculated curve.

Optical Microscopy and Scanning Electron Microscopy: These techniques will be used to image the surface of LB and SA films and to image damage to the pin on the pin-on-disk tribometer before and after friction measurements. For LB and SA films optical microscopy in the polarized and interference modes has been useful in studying the size, shape, and orientation of domains. Decoration techniques have helped to enhance visualization of microdefects in the films. Scanning electron microscopy has a much higher resolution than optical microscopy because it uses an electron beam to image the surface of materials. Back scattered electrons as well as secondary electrons emitted by the sample are detected and used to recreate the surface topology of samples.

Scanning Tunneling Microscopy: This technique will be used to measure an average surface roughness of the substrates used for the LB and SA films. This technique, which has the ability to image individual surface atoms or molecules, requires that the sample is conductive and that the atoms or molecules on the surface have limited mobility. The STM uses an atomically sharp tip to raster across the surface of a sample. If a small potential is applied to the tip, a tunneling current between the surface atoms and the tip develops. This tunneling is due to overlapping of the wave functions of the tip and surface atoms. Generally to produce an image the current is kept constant and the height of the tip is adjusted as the tip moves over the surface. The image so obtained is a map of the tip height z versus the lateral coordinates x and y.<sup>11</sup>

## **AVAILABILITY OF RESEARCH FACILITIES**

All equipment are available at the Institute of Materials Science, University of Connecticut.

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# FIGURE 2: Molecular Structures for PBD, PIP and PDMS Functionally-Terminated Oligomers.

-(CH2-CH=CH-CH2)

1,4 polybutadiene

-(CH<sub>2</sub>-C=CH-CH<sub>2</sub>-)<sub>n</sub> CH<sub>3</sub>

1,4-polyisoprene

1,2-polybutadiene

1,2-polyisoprene

CH<sub>3</sub> COOH-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>F Si - O <del>Jn</del> CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-COOH CH<sub>3</sub>

Di-acid Terminated PDMS